Directed Self-assembly of Metal Oxide Nanodots: Cu_2O on $SrTiO_3$ (100)

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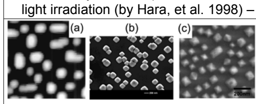
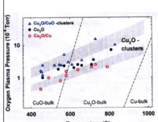
Introduction

- Cu_2O QD is a candidate to study Bose-Einstein condensation.
- Photocatalytic decomposition of water on Cu_2O under visible light irradiation (by Hara, et al. 1998) – H for fuel cells



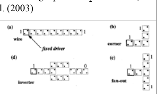
Cu_2O QDs formed epitaxially on single crystal substrates (a) Cu_2O on $SrTiO_3$, by Lyubinetsky et al. (2003), (b) Cu_2O on InP, by Run et al. (2003) and (c) Cu_2O on $LaAlO_3$ by Zhang et al. (2004).



As with QD self-assembly in Ge/Si, metal oxide formation on a planar surface appears to be quasirandom.

Phase diagram to generate single phase Cu_2O nanodots, by Lyubinetsky et al. (2003)

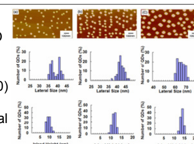
The need for position control:
- Random to reproducibility
- Better control of density & periodicity
- Passive to active nanostructures
- Potential applications: QCA, QD lasers.



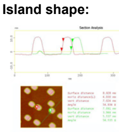
Examples of simple QCA arrays for Boolean logic, Porod, (1998).

OPA-MBE Growth of Self-assembled Cu_2O QDs

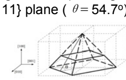
Epitaxial growth:
AFM images after 3, 7, 14 Å Cu_2O deposition and corresponding size and height distributions.
HRXRD: Cu_2O (100) // $SrTiO_3$ (100)
Process conditions:
700 °C, 1.1×10^{-5} Torr oxygen partial pressure.



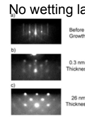
Island shape:



AFM scan shows 53° side angle, corresponding to {111} plane ($\theta = 54.7°$)

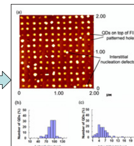


RHEED:
No wetting layer



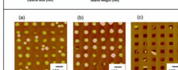
Ideal for directed self-assembly:
- Relatively narrow size distribution. (for predictable properties)
- Initially, island size changes slowly with thickness. (same as abv)
- Initially, island density increase with thickness. (density control)
- Island size depends exponentially on T. (size control)

Directed Self-assembly : nano-scale patterning



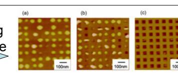
Best result: (a) AFM image showing the preferential growth of Cu_2O islands on top of the FIB implant zones, and (b) the size and height distribution.

Process conditions: 167 nm spacing pattern, 6.2×10^3 ions/spot, (10 FIB scans), 700 °C, 7 Å



167 nm, 5, 10, 50 FIB scans

Spacing decrease

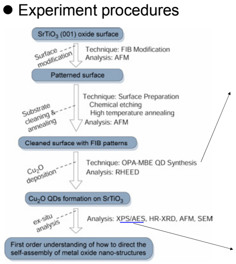


130 nm, 5, 10, 50 FIB scans

Comparison results: (on the same sample)
- FIB modification spots are always the preferred nucleation sites.
- Island size is much larger and comparable to that of patterned pit.
- FIB created pits appear to be the sink for migrating adatoms.
- Island density is closely related with "actual" amount of material.
- Continuous deposition after saturation will result in "extra" islands.
- Dose, spacing, and thickness can be tailored to get best results.

Experiment Details

- **Expectations**
  Achieve lateral positioning of QDs by growth on FIB patterned substrate.
- **Experiment procedures**



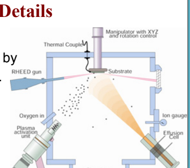
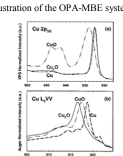


Illustration of the OPA-MBE system

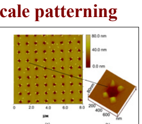


XPS $2p_{3/2}$ (a) and AES Cu $L3VV$ (b) spectra were used to confirm the Cu_2O stoichiometry. From Lyubinetsky, *et al.* J. Appl. Phys., 2003

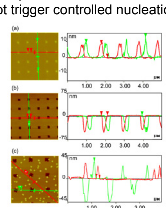
- **Challenges**
  Formation of single phase Cu_2O.
  Find growth temperature that lead to desirable island size.
  Create compatible FIB patterns comparable to the dot density.

Directed Self-assembly : micro-scale patterning

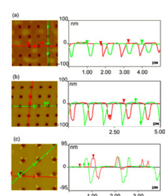
Best result: (a) AFM image showing the preferential growth of Cu_2O islands on the edges of the FIB implant zones, (b) a higher resolution scan of one FIB implant zone.
Process conditions: 1 μm spacing pattern, 725 °C, 7 Å film thickness



Comparison results: On the same sample, lower dosage (left) did not trigger controlled nucleation.



AFM image and line scan of (a) a substrate region following FIB modification. Ion density was 5.63×10^{16} ions/cm^2 with 4.43×10^6 Ga ions on each spot. (b) the same region after substrate etching and annealing. (c) after nanodot synthesis.



AFM image and line scan of (a) a region following FIB modification. Ion density was 5.63×10^{18} ions/cm^2. (b) the same modified region after substrate etching and annealing, (c) the same region after nanodot synthesis.

Y. Du, *et al.*, (2004). *Appl. Phys. Lett.*, **84**(25), 5213.

Conclusions and Discussions

- We have demonstrated that there are two ways to guide the growth of Cu_2O nanodots on $SrTiO_3$ (100) substrates.
- Under certain oxygen plasma assisted molecular beam epitaxy growth conditions, it was then possible to grow Cu_2O immediately adjacent to or on top of the FIB modified zone.
  - For the larger topographical features (corresponding to higher Ga+ doses), Cu_2O nanodots were found to grow at the edge of the induced topography.
  - For the smaller topographical features and smaller FIB pattern spacing, Cu_2O nanodots were found to grow directly on top of the topography.
- More detailed study of the influence of FIB surface modification upon nanodot growth location is needed to understand the fundamental factors motivating guided growth.
- The surface and interface chemistry, topography, defect structure, and / or stress surrounding each of the FIB modified regions are possible motivators of the different growth patterns.
- The ability to guide the growth of metal oxide nanodots raises the prospect of incorporating the useful properties of metal oxides into a host of engineered devices for nanoelectronics, spintronics and other high-performance applications.

Acknowledgements

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